



Synthesis, characterisation and catalytic performance of nanocrystalline Co_3O_4 for gas-phase chlorinated VOC abatement

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ABSTRACT

Several nanocrystalline Co_3O_4 catalysts were investigated for their activity and selectivity during the oxidation of 1,2-dichloroethane, which was selected as a model chlorinated volatile organic compound. A wide number of synthesis routes starting from cobalt(II) nitrate were examined, namely calcination of the precursor salt, solid-state reaction, precipitation and sol-gel. The catalysts prepared by precipitation decomposed the chlorinated feed at the lowest temperatures. Activity was observed to be chiefly governed by a small crystallite size which may give rise to more easily accessible active sites (oxygen O^- or O^{2-} species), which were not present on the more highly crystalline Co_3O_4 catalysts. Additionally, surface Lewis acidity played a relevant catalytic role. Interestingly, the behaviour of some of the nanocrystalline oxides was superior to that of supported noble metal catalysts and other bulk oxide catalysts. Conversion to deep oxidation products was complete (CO_2 , HCl and Cl_2), and no appreciable deactivation with time on stream was noticed.

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1. Introduction

Over the past several years, environmental legislation has imposed increasingly stringent limits on permitted atmospheric emission levels. In particular, the release of volatile organic compounds (VOCs) has received much attention. VOCs are a widely ranging class of chemicals commonly occurring in many commercial waste streams and containing over 300 compounds. Their release has widespread environmental implications and has been linked to the increase in photochemical smog, the depletion in atmospheric ozone and the production of ground-level ozone. Additionally, many VOCs have highly noxious effects on human health. The emission sources associated with industrial activity (manufacture of organic chemicals and polymers, vent air from operations in which VOCs are used for cleaning and degreasing purposes in metal processing, machining and finishing, and exhaust air from ground water and/or soil remediation processes) reveal a wide variety of compounds with different chemical compositions, though the ease or difficulty involved in removing them varies considerably. In this sense, chlorinated VOCs, which have enjoyed widespread acceptance as reagents and solvents due to their compatibility with most substrate materials and non-flammability, are, on account of their high stability, amongst the most difficult to abate compounds by catalytic combustion.

An alternative to commonly applied but expensive noble metals is transition metal oxides. Despite their high activity for the abatement of chlorinated VOCs, the disadvantages associated with noble metals (high cost, low thermal stability and susceptibility to poisoning [1]) cannot be overcome. Thus, substantial efforts are currently being made to develop transition metal oxides catalysts with a comparable activity. Cobalt oxide catalysts are effective low-temperature combustion catalysts of non-chlorinated hydrocarbons [2–5], carbon monoxide [6,7] and diesel soot [8]. However, much less consideration has been given to investigating the applicability of this class of catalysts for the gas-phase oxidation of chlorinated VOCs [9,10].

The active behaviour of Co-based catalysts in the above applications, typically as Co_3O_4 , is most likely related to high bulk oxygen mobility and the facile formation of highly active oxygen (O^- or O^{2-}) species. These properties are mainly related to crystallite size. Hence, the controlled preparation of Co_3O_4 nanoparticles (1–50 nm) has attracted considerable interest owing to its impact on governing their ultimate performance and applications. In the present work, the suitability of cobalt oxide catalysts for the abatement of chlorinated VOCs was investigated. Particularly, the catalytic behaviour of nanocrystalline Co_3O_4 systems on the total oxidation of 1,2-dichloroethane, which was chosen as a model chlorinated VOC, was examined in a fixed-bed flow reactor. 1,2-Dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$, DCE), also known in the industry as ethylene dichloride (EDC), is probably one of the most important chlorinated VOCs emitted in gaseous industrial waste streams since it is used as an intermediate for the production of polyvinyl

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chloride, the most produced plastic in the world after polyethylene. Less important uses are as a solvent in textile cleaning and metal degreasing and paint remover, a starting material for paint, varnish, and finish removers, a cleaner for upholstery and carpets, a fumigant, a lead scavenger in antiknock gasoline and as a dispersant for plastics and elastomers such as synthetic rubber.

2. Experimental

2.1. Catalyst preparation

A number of routes including thermal decomposition, solid-state reaction, wet-chemical and sol-gel methods were employed to synthesise bulk cobalt oxide catalysts. Firstly, Co_3O_4 was prepared by simple calcination in air of the selected cobalt precursor (hexahydrated cobalt(II) nitrate, Sigma-Aldrich). This catalyst was denoted as DC. Secondly, the cobalt oxide was prepared by solid-state reaction following two different procedures. Hence, on one hand, the GB catalyst was prepared by grinding a mixture of cobalt(II) nitrate (9 g) with ammonium hydrogen carbonate (Fluka) (6.1 g) with a molar ratio of 2:5 in an agate mortar for 30 min [11]. The solids were washed thoroughly with distilled water and collected by filtration. The GC catalyst was obtained by grinding a mixture of citric acid (5.3 g) (Sigma-Aldrich) with the Co(II) basic carbonate precursor (8.7 g) (Sigma-Aldrich) [12]. The mixture was first premixed by hand grinding for 5 min. The grinding was then carried out in a planetary ball mill (Retsch) at a speed of 600 rpm for 6 h. The as-ground citrate precursors were collected and washed thoroughly.

Co_3O_4 catalysts were also prepared by wet-chemical methods. The first route (OW) consisted of a precipitation-oxidation reaction in an aqueous solution. The precipitation process was conducted by the drop-by-drop addition of 100 ml of a 3.2 M solution of NaOH (Sigma-Aldrich) into an aqueous solution (50 cm^3) of 0.6 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 50 °C. Next, 100 ml of H_2O_2 (Sigma-Aldrich, 50 wt.%) was also introduced drop-by-drop under constant stirring [13]. The precipitate was then filtered and washed with deionised water. The alternative procedure (CC) involved an aqueous hydroxycarbonate precipitation [12]. Thus, a 1.2 M aqueous (200 cm^3) solution of Na_2CO_3 (Fluka) was added into a 0.5 M aqueous (100 cm^3) solution of cobalt(II) nitrate under vigorous stirring. The temperature was kept at 80 °C during the precipitation (0.5 h), the pH was fixed at 8.5 and the precipitates were collected and washed thoroughly. Finally, a sol-gel method (SG) was employed. The oxide was prepared by an aqueous sol-gel citrate procedure involving complexation of cobalt(II) nitrate (0.1 M, 250 cm^3) and citric acid. An excess of citric acid (3.5 g) was used to ensure complete complexation. Water was removed on a rotary evaporator at 40 °C until the formation of a gel or viscous material. The temperature was then increased up to 70 °C and maintained overnight. A spongy, highly hygroscopic, amorphous citrate was obtained [14].

All the catalyst precursors were dried at 110 °C overnight and then calcined at 300 or 500 °C in static air for 4 h at a heating rate of 1 °C min^{-1} . For the samples calcined at 500 °C, an intermediate calcination at 300 °C for 0.5 h was performed. Next, catalyst pellets with a 0.3–0.5 mm diameter were prepared by a process of compressing the oxide powders into flakes in a hydraulic press (Specac), crushing and sieving. All samples obtained prior to catalytic activity and selectivity experiments were characterised using several analytical techniques.

2.2. Characterisation techniques

Textural properties were evaluated from the nitrogen adsorption-desorption isotherms, determined at –196 °C with a Microm-

eritics ASAP 2010 apparatus. The specific areas of the samples were determined in line with standard BET procedure, using nitrogen adsorption taken in the relative equilibrium pressure interval of 0.03–0.3. Mean pore size was calculated using the BJH method. The samples were previously degassed overnight under high vacuum conditions. X-ray diffraction (XRD) studies were conducted on a X'PERT-MPD X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and Ni filter. The X-ray tube was operated at 30 kV and 20 mA. Samples were scanned between 20° (2θ) and 70° (2θ), and the X-ray diffraction line positions were determined with a step size of 0.02° and a counting time of 2.5 s per step. Phase identification was conducted by comparison with JCPDS (Joint Committee on Powder Diffraction Standards) database cards. The thermo-oxidative degradation of the cobalt precursors was investigated by means of dynamic thermogravimetry using Setaram Setsys Evolution apparatus under atmospheric pressure. The mass loss and the sample temperature were continuously recorded by a computerised data acquisition system. The studies were carried out from 25 to 550 °C at a constant heating rate of 10 °C min^{-1} . The oxidant stream was dry air (50 $\text{cm}^3 \text{ min}^{-1}$) flowing downwards onto the cylindrical sample holder.

Raman spectra, acquired using a Leica 50× N Plan (0.75 aperture) lens, were recorded with a Renishaw InVia Raman spectrometer coupled to a Leica DMLM microscope. The spectrometer was equipped with a 514-nm laser (ion-argon laser, Modu-Laser) with a nominal power at the source of 50 mW, with maximum power at the sample of 20 mW. Ten seconds were employed for each spectrum, and 20 scans were accumulated with 10% of the maximum power in the spectral window from 150 to 1150 cm^{-1} .

Temperature-programmed desorption (TPD) of ammonia was performed on a Micromeritics AutoChem 2920 instrument equipped with a quartz U-tube coupled to a thermal conductivity detector. Prior to adsorption experiments, the samples were first pre-treated in a 5% O_2 /He stream at 500 °C and then cooled to 100 °C in a He flow (20 $\text{cm}^3 \text{ min}^{-1}$). Later, the NH_3 adsorption step was performed by admitting a flow of 10% NH_3 /He at 100 °C up to saturation. Subsequently, the samples were exposed to a flow of helium (50 $\text{cm}^3 \text{ min}^{-1}$) for 1 h at 100 °C to remove reversibly and physically bound ammonia from the surface. Finally, desorption was carried out from 100 to 500 °C at a heating rate of 10 °C min^{-1} in an He stream (50 $\text{cm}^3 \text{ min}^{-1}$). This temperature was maintained for 1 h until the adsorbate was completely desorbed. The amount of gases desorbed was determined by time integration of the TPD curves. Diffuse reflectance (DRIFT) spectra of pyridine adsorbed on the oxide samples were obtained with a Nicolet Protegé 460 ESP spectrometer, equipped with a Spectra-Tech high-temperature chamber and a nitrogen-cooled MCT detector. All spectra were recorded in the range 1700–1300 cm^{-1} averaging 400 scans with a 1 cm^{-1} resolution and analysed using OMNIC software. After the sample was evacuated at 550 °C under high vacuum conditions for 1 h, pyridine was admitted at 200 °C at the equilibrium pressure of 3 mbar. After removing physisorbed pyridine, the spectra were then recorded. Difference spectra were obtained by subtracting the spectrum of the clean sample from the spectra obtained after pyridine adsorption.

Redox behaviour was examined by temperature-programmed reduction (TPR), and the experiments were also conducted on a Micromeritics AutoChem 2920 instrument as well. Firstly, all the samples were pre-treated in an oxygen stream (5% O_2 /He) at 500 °C for 1 h and then cooled to room temperature. The reducing gas used in all experiments was 5% H_2 /Ar, with a flow rate of 50 $\text{cm}^3 \text{ min}^{-1}$. The temperature range explored was from room temperature to 500 °C, with a heating rate of 10 °C min^{-1} . This temperature was maintained for 0.5 h. The water produced by reduction was trapped in a cold trap, and consumption of H_2 was quantitatively measured by time integration of the TPR profiles.

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